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Global modelling of secondary organic aerosol in the troposphere: A sensitivity analysis

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Abstract

A global 3-dimensional chemistry/transport model able to describe O_3, NO_x, Volatile Organic Compounds (VOC), sulphur and NH_3 chemistry has been extended to simulate the temporal and spatial distribution of primary and secondary carbonaceous aerosols in the troposphere focusing on Secondary Organic Aerosol (SOA) formation. A number of global simulations have been performed to determine a possible range of annual global SOA production and investigate uncertainties associated with the model results. Uncertainties in the model calculations related to the enthalpy of vaporization, the solubility and the activity coefficient of the condensable species, the chemical fate of the first generation low volatility oxidation products, the ageing of particles with regard to their hydrophilic properties, the partitioning of SOA on various aerosol surfaces and the evaporation of semi-volatiles from aerosol surfaces have been evaluated. Although not all sources of uncertainties have been investigated, according to our calculations, the above factors within the experimental range of variations could result to an overall uncertainty of about a factor of 20 in the global SOA budget. The global annual SOA production from biogenic VOC might range from 2.5 to 44.5 Tg of organic matter per year, whereas that from anthropogenic VOC ranges from 0.05 to 2.62 Tg of organic matter per year. These estimates can be considered as a lower limit, since partitioning on coarse particles like nitrate, dust or sea-salt, together with the partitioning and the dissociation of the semi-volatile products in aerosol water has been neglected. The large uncertainties associated with the emissions of VOC have not been investigated in this study. Comparison of model results to observations, where available, shows a better agreement for the upper budget estimates than for the lower ones.

1. Introduction

Atmospheric aerosols act as substrates for heterogeneous reactions and affect tropospheric chemistry (Dentener and Crutzen, 1993). Aerosols can also back scatter or

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absorb solar radiation modifying therefore the radiative state of the atmosphere (IPCC, 2001). Black carbon aerosols are heating the atmosphere by absorption of solar radiation, whereas the other aerosol constituents like organic aerosols are cooling the Earth's atmosphere. Due to their longer lifetimes than larger particles, fine aerosols are transported far from their source regions and are thus expected to have stronger climatic impact than larger particles. The $PM_{2.5}$ fraction of them can also damage human health (Jones, 1999; Harrison and Yin, 2000). Hydrophilic aerosols can act as condensation nuclei (CN) and even cloud condensation nuclei (CCN), having thus an indirect climatic effect by modification of cloud properties (Novakov and Penner, 1993; Novakov and Corrigan, 1996). Organic material significantly contributes to the total fine aerosols by ~20–50% at continental mid-latitudes (Saxena and Hildemann, 1996) and as high as 90% in tropical forested areas (Andreae and Crutzen, 1997; Talbot et al., 1988, 1990; Artaxo et al., 1988, 1990). A substantial fraction of the organic component of atmospheric particles consists of water-soluble, possibly multifunctional compounds (Saxena and Hildemann, 1996; Facchini et al., 1999).

Andreae and Crutzen (1997) have suggested that the production of organic aerosols from the oxidation of biogenic organic compounds might ranges from 30 to 270 $Tg\,yr^{-1}$ and thus can be comparable in magnitude to the production of biogenic and anthropogenic sulphate aerosols (Pandis et al., 1992). Laboratory studies have shown that mainly ozonolysis, and to a smaller extent oxidation by OH and NO_3 radicals of several biogenic compounds like α- and β-pinene produces organic substances, which can condense onto particulate phase (Hoffmann et al., 1997; Griffin et al., 1999a; Christoffersen et al., 1998). Aromatic compounds emitted from human activities can also contribute to the chemical formation of organic particulate matter (Odum et al., 1997). Griffin et al. (1999b) performed an exploratory study of the present-day Secondary Organic Aerosol (SOA) formation from the oxidation of biogenic Volatile Organic Compounds (VOC) and estimated a global production of SOA of 13–24 $Tg\,yr^{-1}$. Kanakidou et al. (2000) calculated that this source of SOA has increased from 17–28 $Tg\,yr^{-1}$ in pre-industrial times to 61–79 $Tg\,yr^{-1}$ at present. This 3-4-fold enhancement of the for-

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mation of organic aerosol from biogenic VOC has been attributed to an increase in ozone and primary organic aerosol from anthropogenic sources. Recently, Chung and Seinfeld (2002) re-evaluated the present-day SOA formation at 11.2 $Tg\,yr^{-1}$ whereas Derwent et al. (2003) estimated a higher global SOA production of 63 $Tg\,yr^{-1}$.

Knowledge on the formation and properties of SOA and their spatial and temporal variability is far from being satisfactory, although it is needed to evaluate their environmental impact. Therefore, a careful identification of the critical gaps in our knowledge is needed to allow further research to highlight the aerosol impact on chemistry and climate. In this perspective, the present study focuses on the estimate of the mass distribution of SOA and the identification of physicochemical processes that have not been satisfactorily addressed in previous studies and are shown to be critical for these calculations. It also addresses the importance of anthropogenic versus the natural component of SOA.

2. Model description

The model used for the present study is the well-documented off-line chemical transport model TM3 (Houweling et al., 1998; Dentener et al., 1999; Jeuken et al., 2001). This model version has a horizontal resolution of $3.75^{\circ} \times 5^{\circ}$ in latitude and longitude, and 19 vertical hybrid layers from the surface to 10hPa. Roughly, 5 layers are located in the boundary layer, 8 in the free troposphere and 6 in the stratosphere. The model's input meteorology varies every 6 h and comes from the ECMWF ERA15 re-analysis data-archive for the year 1990 (Gibson et al., 1997; http://www.ecmwf.int/data/era/html).

2.1. Emissions

For the biogenic VOC emissions, the Global Emission Inventory Activity (GEIA) database (Guenther et al., 1995) and the Emission Database for Global Atmospheric Research (EDGAR) version 2.0 database (Olivier et al., 1996), both for the year 1990

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have been adopted.

According to the GEIA database (Guenther et al., 1995) about 127 Tg C (1 Tg = 10^{12} g) of monoterpenes are being emitted annually in the atmosphere. Other Reactive Volatile Organic Compounds (ORVOC) are being emitted by about 260 Tg C yr^{-1}. 32% of them are assumed to be able to produce particles (Griffin et al., 1999b).

The emissions of aromatic hydrocarbons adopted here (EDGAR database; Olivier et al., 1996) consist of 6.7 Tg yr^{-1} of toluene, 4.5 Tg yr^{-1} of xylene, 0.8 Tg yr^{-1} of trimethylbenzene and 3.8 Tg yr^{-1} of other aromatics (except benzene, which is not able to form particles; Odum et al., 1997). Primary emissions of carbonaceous aerosols from fossil fuel are taken from Cooke et al. (1999) and consist of 5.1 Tg yr^{-1} Black Carbon (BC) and 7.0 Tg yr^{-1} Organic Carbon (OC) for the primary organic aerosol (POA). For the biomass burning primary emissions of carbonaceous aerosols from tropical forests we have adopted the Cooke and Wilson (1996) estimate of 6.0 Tg yr^{-1} for BC, while for POA we use an annual flux of 12.5 Tg OC yr^{-1}, that results from the fossil fuel to biomass burning emission ratio given by Liousse et al. (1996) estimates which was applied to Cooke et al. (1999) inventory. Temperate and boreal forests emit annually 6.1 Tg OC and 2.9 Tg BC, by assuming that POA emissions are 12.3% of the temperate and boreal CO emissions, whereas BC is 5.9%. In the case of POA, 50% of the emitted particles are assumed to be hydrophilic; in the case of BC, 20% of the total emissions are assumed hydrophilic (Chung and Seinfeld, 2002). In our model, these primary particles serve as pre-existing aerosol for the condensation of the chemically formed low volatility compounds, both from biogenic and anthropogenic hydrocarbons.

2.2. Gas-phase chemistry

The model uses a modified version of the Carbon Bond Mechanism 4 (CBM-4) chemical mechanism (Gery et al., 1989) to simulate global atmospheric chemistry as described in detail by Houweling et al. (1998), together with sulphur and ammonia chemistry (Dentener et al., 1999; Jeuken et al., 2001). For the present study, reactions of terpenes and aromatics have been included to affect both gas-phase chemistry and

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aerosol production. The α- and β-pinene represent the two biogenic SOA precursor VOC (Kanakidou et al., 2000), while toluene and xylene represent the two anthropogenically emitted aromatic compounds that form SOA (Odum et al., 1997). This lumping is justified by the missing knowledge on the molecular composition of the biogenic and anthropogenic organic emissions and their fate, together with the enormous number of compounds present in the SOA. The lack of data on the gas-phase removal parameters and on the SOA formation yields for most of the organic substances, and on their oxidation products is also implying the lumping of the atmospheric precursors of SOA. Similar approaches with different number of surrogate compounds have been used in previous studies (Griffin et al., 1999b; Kanakidou et al., 2000; Chung and Seinfeld, 2002; Derwent et al., 2003).

A two-product model approximation, which has been shown to be the simplest way to efficiently represent aerosol formation both from biogenic (Hoffmann et al., 1997) and aromatic VOC (Odum et al., 1997), is being used to represent SOA formation online with the VOC gas-phase:

$$\text{VOC} + \text{oxidant} \rightarrow a_1 P_1 + a_2 P_2 + \text{high volatility products}. \quad (1)$$

Where a_i is the mass-based stoicheiometric coefficient of the low volatility product P_i that partitions between the gas and particulate phase with a partitioning coefficient K_i.

P_i can further oxidize to gas-phase high-volatility products and second generation low volatility surrogate compounds B_i. This oxidation chain can continue until either full oxidation (down to CO, CO_2, etc.) or removal of the gaseous or/and the aerosol phase species from the system by wet and dry deposition. As a first approximation, and because the oxidation pathways and products of the second generation species are almost totally unknown, we assume that the second generation products considered only in case S1.3 are stable enough to have slow oxidation rates in the gas-phase. This assumption is being supported by the fact that the second generation products (B_i) are expected to have more functional groups than the first generation products (P_i) and thus to be enough low-volatile to reside most of their lifetime in the particulate phase.

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Therefore, in this sensitivity study discussed in Sect. 3.2.2, all biogenic first generation semi-volatile products are considered to oxidize down to similar bulk species B_b, while the anthropogenic ones oxidize to B_a. These species (B_a, B_b) are not further oxidized, and are removed from the atmosphere only by wet and dry deposition. Note however that possible reactions of P_i and B_i products in aerosols leading to modification of the chemical composition and the mass of the aerosol have been neglected in the present study due to missing knowledge.

For carbon balance purposes the following mass-based stoicheiometric reactions are taken into account, by assuming that the products of biogenic VOC that are able to partition between gas and aerosol phase are similar to known terpene products (Christoffersen et al., 1998; Calogirou et al., 1999; Cocker III et al., 2001a):

$$\alpha\text{–pinene} + O_3 \rightarrow a_1(\alpha\text{–pin–}P_1) + a_2(\alpha\text{–pin–}P_2) + 2\cdot(X - a_1 - a_2)(RO_2) \quad (2)$$

$$\beta\text{–pinene} + O_3 \rightarrow a_1(\beta\text{–pin–}P_1 + HCHO) + a_2(\beta\text{–pin–}P_2 + HCHO) + 2\cdot(X - a_1 - a_2)(RO_2) \quad (3)$$

$$\alpha\text{–pin–}P_1 + \text{oxidants} \rightarrow ALD2 + B_b \quad (4)$$

$$\alpha\text{–pin–}P_2 + \text{oxidants} \rightarrow ALD2 + B_b \quad (5)$$

$$\beta\text{–pin–}P_1 + \text{oxidants} \rightarrow HCHO + B_b \quad (6)$$

$$\beta\text{–pin–}P_2 + \text{oxidants} \rightarrow HCHO + B_b \quad (7)$$

Where RO_2 is further treated in CBM4 as the corresponding radical formed during isoprene oxidation and ALD2 is a lumped aldehyde product as in the original CBM4 mechanism (Gery et al, 1989; Houweling et al., 1998). X denotes the ratio of the molecular weight of the parent VOC to the molecular weight of the condensable products. The factor 2 applies to the carbon balance conservation. Reactions (4), (5), (6) and (7) are considered only for the sensitivity study shown in Sect. 3.2.2. The reactions of biogenic VOC with OH and NO_3 radicals are considered, but any particulate matter

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formation from these reactions is neglected in the present study. This assumption is not expected to be critical for the outcome of the study, since it is known that low volatile compounds are formed mainly from O_3 reactions with biogenic VOC (Hoffmann et al., 1997). For simplicity, these OH and NO_3 reactions are assumed to exclusively produce RO_2 radicals that follow the isoprene oxidation chain. This assumption will need to be improved in the future.

A similar approach is followed for aromatic hydrocarbons, by assuming that the products that are able to partition are similar to known semi-volatile compounds (Forstner et al., 1997; Cocker III et al., 2001b):

$$\text{toluene} + \text{OH or } O_3 \rightarrow a_1(\text{tol}-P_1) + a_2(\text{tol}-P_2 + \text{Methylglyoxal}) + 7\cdot(X - a_1 - a_2)\text{PAR}, \quad (8)$$

$$\text{xylene} + \text{OH or } O_3 \rightarrow a_1(\text{xyl}-P_1) + a_2(\text{xyl}-P_2 + \text{Methylglyoxal} + \text{PAR}) + 8\cdot(X - a_1 - a_2)\text{PAR}, \quad (9)$$

$$\text{tol}-P_1 + \text{oxidants} \rightarrow B_a, \quad (10)$$

$$\text{tol}-P_2 + \text{oxidants} \rightarrow B_a, \quad (11)$$

$$\text{xyl}-P_1 + \text{oxidants} \rightarrow B_a, \quad (12)$$

$$\text{xyl}-P_2 + \text{oxidants} \rightarrow B_a, \quad (13)$$

where PAR is paraffinic carbon as in the original CBM4 mechanism (Gery et al., 1989, Houweling et al., 1998). The factors 7 and 8 apply to the carbon balance conservation. Reactions (10), (11), (12) and (13) are considered only for the sensitivity study shown in Sect. 3.2.2. The reactions of aromatics with NO_3 radicals are considered producing only high volatility products represented in the model by appropriate number of PAR. The adopted rates for the reactions (2)–(13) are shown in Table 1.

2.2.1. Aerosol formation – factors of uncertainty

Assuming an equilibrium partitioning into an absorptive organic matter phase (Pankow, 1994a; Pankow, 1994b; Odum et al., 1996), the equilibrium between the gas and the

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aerosol phase of a condensable species i that is produced from VOC oxidation and can partition between the two phases, is governed by:

$$G_i = \frac{A_i}{K_i M_o}, \tag{14}$$

where G_i, A_i is the gas and the aerosol phase concentration of the species i in ng m^{-3}, respectively, K_i is the partitioning coefficient of the species, in m^3 μg^{-1}, and M_o is the total particulate phase concentration in μg m^{-3}:

$$M_o = PP + \sum_i A_i, \tag{15}$$

where PP is the mass (in μg m^{-3}) of the primary particles that can serve as absorptive medium. The partitioning coefficient K_i of the oxidation product P_i, is described by (Pankow, 1994a; Pankow, 1994b):

$$K_i = \frac{760RTf}{MW10^6\zeta_i p^0_{L,i}}, \tag{16}$$

where R is the gas constant, f is the mass fraction of the total suspended particulate matter that acts as the absorbing phase, MW is the mean molecular weight of the absorbing matter, ζ_i is the activity coefficient of compound i in the particulate phase, $p^0_{L,i}$ is the vapour pressure of the compound i in temperature T and the factors 760 and 10^6 apply for the conversion of units. Assuming that f and MW remain constant, the changes in K_i with temperature can be calculated by applying the Clausius-Clapeyron equation (Atkins, 1990):

$$\frac{d\ln p^0_{L,i}}{dT} = \frac{\Delta H_i}{RT^2}, \tag{17}$$

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where ΔH_i is the enthalpy of vaporization of the compound i. By combining (16) with (17) we get:

$$K_i^T = K_I^{T_{SC}} \frac{1}{\zeta_i} \frac{T}{T_{SC}} \exp\left[\frac{\Delta H_i}{R}\left(\frac{1}{T} - \frac{1}{T_{SC}}\right)\right], \quad (18)$$

where ΔH_i is the partitioning coefficient K_i at temperature T, and $K_i^{T_{SC}}$ is the smog chamber measured value of K_i at temperature $T_{SC} = 298$ K. The value of ΔH is highly uncertain and variable between species, and strongly affects the value of K_i (Fig. 1).

The activity coefficient ζ_i of the individual components may change with time as a function of the chemical composition of the particulate phase. To take this into account, the multicomponent Wilson equation has to be used (Prausnitz, 1969; Bowman and Karamalegos, 2002):

$$\ln\zeta_i = 1 - \ln\left(\sum_j x_j \Lambda_{ij}\right) - \sum_k \frac{x_k \Lambda_{ik}}{\sum_j x_j \Lambda_{jk}} \quad (19)$$

where x_i is the mole fraction of the component i, Λ_{ij}, Λ_{ik} and Λ_{jk} are parameters representing the interactions between the compounds i and j, i and k and j and k, respectively, and all summations are over all species. For simplicity, component interactions are assumed symmetrical ($\Lambda_{ij} = \Lambda_{ji}$). The Λ values for the different species present in the carbonaceous aerosols (Table 2) have been selected on the base of the expected chemical similarity of the species and lie within the range suggested by Bowman and Karamalegos (2002). In this manner, all secondary organic species are assumed to behave alike between them and quite similar to the hydrophilic primary organics. The hydrophobic primary organics behave less similar to the secondary organics. All organic aerosol species are not so similar to the hydrophobic particulate black carbon particles, while the hydrophilic black carbon fraction is quite similar to the hydrophilic organic particles. In Table 2, Λ values are also given for sulphuric and ammonia aerosol on which SOA could also partition.

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While the concentration of A_i varies, M_o also changes (15). If we assume that the total amount of semi-volatile products (both aerosol and gas-phase) repartition in each timestep, then the aerosol concentration of each species is given by:

$$A_I = \frac{\left(A_i^0 + G_I^0 + \Delta G_i^p\right) K_i M_o}{1 + K_i M_o}, \quad (20)$$

where G_i^0 and A_i^0 are the concentrations of the species i in the gas and the aerosol phase, respectively in the previous timestep and ΔG_i^p is the change in the gas-phase concentration of the species i due to chemical production (all products) and destruction (first generation products) in the current timestep. This approach gives an upper limit for the evaporation process, since it assumes that all SOA evaporates from the particle at each timestep. This will underestimate the aerosol mass concentration. By solving the mass balance Eq. (15) using Eq. (20) we can calculate iteratively the value of M_o. Then the aerosol concentrations can be derived from M_o using Eq. (20) and subsequently the gas-phase concentration of the species i by applying Eq. (14).

When neglecting evaporation of the particles, Eq. (20) that gives the new aerosol concentration is modified to:

$$A_i = A_i^0 + \frac{\left(G_i^0 + \Delta G_i^p\right) K_i M_o}{1 + K_i M_o}. \quad (21)$$

M_o is calculated iteratively based on Eqs. (15) and (21). Then, the aerosol concentration A_i is calculated by Eq. (21) and the gas-phase concentration G_i by:

$$G_i = G_i^0 + \Delta G_i^p - \frac{\left(G_i^0 + \Delta G_i^p\right) K_i M_o}{1 + K_i M_o} = \frac{\left(G_i^0 + \Delta G_i^p\right)}{1 + K_i M_o}. \quad (22)$$

As mentioned in Sect. 2.2, SOA formation from biogenic VOC oxidation initiated by OH is of minor importance relative to that by O_3 and is neglected here. In addition, SOA

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formation by NO_3 radical reactions with VOC, although occurring, is poorly studied and thus also neglected in the present work. These assumptions lead to an underestimation of the global SOA production and need future investigations.

2.2.2. Ageing of primary hydrophobic aerosol

To take into account the ageing of primary carbonaceous aerosol from hydrophobic to hydrophilic, we assume that this process occurs by oxidation of organic material that coats the particles by O_3 as has been observed for soot particles in chamber experiments (Pöschl et al., 2001; Decesari et al., 2002). To parameterize this phenomenon we use the formulation experimentally determined by Pöschl et al. (2001) for soot particles coated by benzo(*a*)pyrene:

$$k = \frac{k_\infty K_{O_3}[O_3]}{1 + K_{O_3}[O_3] + K_{H_2O}[H_2O]}, \quad (23)$$

where K_∞ is the pseudo-first-order decay rate coefficient in the limit of high ozone concentrations and has been experimentally found to be equal to $0.015\,s^{-1}$, K_{O_3} is the adsorption rate coefficient of O_3 that serves as the oxidation medium and K_{H_2O} is the adsorption rate coefficient of H_2O that serves as an inhibitor by competitive adsorption. The adsorption rate coefficients of O_3 and H_2O, are computed following the equation by Pöschl et al. (2001):

$$K_i = \frac{S_{0,i}\omega_i}{4[SS]_S}\tau_i, \quad (24)$$

where $S_{0,i}$ is the sticking coefficient of O_3 and H_2O ($3.3 \cdot 10^{-3}$ and $0.4 \cdot 10^{-3}$, respectively), ω_i is the mean thermal velocity, $[SS]_s$ is the surface concentration of adsorption sites for the studied soot particles and measured to be $5.7 \cdot 10^{14}$ sites cm^{-2} and τ_i is the mean residence time of O_3 and H_2O on particle surface sites, measured to be 5 s and $3 \cdot 10^{-3}$ s, respectively. We assume that the conversion of hydrophobic to hydrophilic

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aerosol occurs when a monolayer of hydrophilic carbonaceous material is formed. To parameterize this phenomenon we adopted a mean aerosol size of 0.25 μm and a monolayer thickness of 2.5 nm from the particle surface.

POA ageing is treated similarly to the ageing process of hydrophobic BC, since the POA contains also aromatic groups (Fuzzi et al., 2001) like those coating the soot particles. The validity of this hypothesis though requires to be experimentally checked.

The thus calculated lifetimes of hydrophobic primary carbonaceous aerosols are shown in Fig. 2. Note that the calculated values are of the same order of magnitude with the values reported by Cooke et al. (1999) for the whole troposphere, and with high spatial differences. In the tropics, where relative humidity is much higher than the mid-latitudes the parameterization based on O_3 oxidation gives higher lifetime for the hydrophobic aerosols, since water inhibits the hydrophobic-to-hydrophilic conversion. Also note that longest lifetimes of hydrophobic aerosol are calculated for areas with low concentrations of ozone, which acts as the oxidation medium for this conversion. In the northern hemisphere the lifetime increases during summer due to increased water vapour concentrations. The simultaneous increase in ozone is not able to reduce the hydrophobic aerosol lifetime since the inverse effect of humidity is stronger. The same applies to the summer of the south hemisphere.

2.3. Wet and dry deposition

The wet deposition of the gas-phase aerosol precursors depends on their solubility in cloud droplets according to their Henry's law coefficients (H). The parent VOCs are poorly soluble and have low Henry's law constants, making their wet deposition negligible. On the contrary, the first generation products are better soluble, since they consist of multi-functional compounds including carbonylic and carboxylic groups, while the second generation products are expected to have even more functional groups. From the compilation of Henry's law coefficients by Sander (1999), $H \approx 10^3 - 10^4$ for monocarboxylic acids and $H \approx 10^6 - 10^8$ M atm^{-1} for dicarboxylic acids. Hence, a Henry coefficient of 10^3 for most first generation products and 10^6 for the secondary

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products has been used, except *a*-pin-P_1, *b*-pin-P_1 and xyl-P_1 that are assumed to be pinonic acid (keto-monocarboxylic acid), pinic acid (dicarboxylic acid) and toluic acid, respectively. For these acids the Henry values have been assumed to be 10^4, 10^6 and 10^4, respectively. The temperature dependence of Henry coefficients is described by (Sander, 1999):

$$\frac{d\ln H}{dT} = \frac{\Delta H_i}{RT^2}, \tag{25}$$

where ΔH_i is the heat of dissolution and equals to −12 K (Sander, 1999) for all compounds. For the dry deposition of the gaseous species, the Ganzeveld and Lelieveld (1995) scheme has been used, which is based on the formulation developed by Wesely (1989). For the aerosol phase, wet and dry deposition is parameterized as suggested by Parungo et al. (1994) and already applied to sulphate particles in the model (Jeuken et al., 2001).

3. The simulations

A number of global simulations have been performed to investigate uncertainties associated with the model results and determine a possible range of annual global SOA production. Several factors of uncertainty in the model calculations have been studied, like the amount and nature of pre-existing absorbing aerosol, the effect of evaporation of semi-volatile products from the particulate phase, the enthalpy of vaporization, the solubility and the activity coefficient of the condensable species, the chemical fate of the first generation low volatility oxidation products and the ageing of particles with regard to their hydrophilic properties. These simulations are summarized in Table 4.

3.1. Impact of the absorbing matter and evaporation

Simulations S1 and S3 (as well as S2 and S4) differ on the amount and nature of the absorbing aerosol phase. S1 considers only the condensation on carbonaceous

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aerosols, while S3 assumes that condensation also occurs on sulphuric (sulphate and methanesulphonate) and ammonium. Simulations S1 and S2 (as well S3 and S4) differ on the consideration of evaporation of pre-existing semi-volatile products.

3.1.1. Calculated SOA distributions

Figure 3 shows the calculated SOA concentrations for the lowest model level (surface), corresponding to both SOA formed during biogenic VOC oxidation (SOAb) and SOA formed during anthropogenic VOC oxidation (SOAa) components, for February and August for the case S1. The calculated concentration of SOA produced from biogenic VOC oxidation exceeds that from anthropogenic one by an order of magnitude and particularly the maximum SOAb is by about 30 times (30 in February, 36 in August) higher than the maximum SOAa concentration. The zonal mean concentrations for February and August, again for the case S1, for SOAb and SOAa are shown in Fig. 4. Both for SOAb and SOAa, the upper troposphere local maximum is due to condensation of the gas-phase compounds transported at these altitudes, where temperatures are very low and thus the partitioning coefficient is high.

The annual production of SOAb is calculated to be higher by more than a factor of 25 than that of SOAa. SOAa contributes to the total SOA concentration from 30% to 65% above and downwind of industrialized areas in the northern hemisphere where its contribution maximizes during winter and becomes less than 15% during summer when biogenic VOC emissions are high. These numbers show that although the global annual SOA production is by far dominated by the biogenic VOC, in industrialized areas during the winter when the emissions of biogenic VOC are very low, the anthropogenic hydrocarbons can contribute significantly to the total secondary organic aerosol.

Similar patterns are calculated for SOA distributions when considering condensation also on sulphuric and ammonium aerosols (cases S3 and S4), and when neglecting the evaporation of pre-existing semi-volatile products from the aerosol phase (cases S2 and S4). The SOA surface distribution of cases S1, S2 and S3 are depicted in Fig. 5 for comparison. Although the patterns are similar, the absolute concentrations

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increase from S1 to S3 to S2 to S4. In particular, the maximum calculated total SOA concentrations for August increase by factors of 1.7, 3.0 and 3.4 for S3, S2 and S4, respectively. In addition, enhancements of SOA concentrations over continental tropics are calculated when evaporation is neglected (cases S2 and S4) due to both the high air temperature favouring evaporation and the vicinity of SOA sources.

3.1.2. Budget calculations

The calculations of the global annual SOA production performed using the results of chamber experiments for the four different cases are summarized and compared with earlier global modelling studies in Table 5. Our model results are within the range of earlier estimates by Griffin et al. (1999b), Kanakidou et al. (2000), Chung and Seinfeld (2002) and Derwent et al. (2003). In order to understand the differences between the different model results, including the present work, we need to compare the different assumptions of the various model approaches. All 5 models follow rather different approaches; they assume different substrates for condensation of SOA, they differ in the consideration of evaporation as well as the surrogate VOC compounds considered to form SOA precursors. To these conceptual particularities of the models, more generally applied technical differences are added like the spatial and temporal resolutions of the models, the parameterizations and input data used to represent transport and wet deposition processes. Such differences have been identified in the past to contribute to large differences in the concentration of radionuclides and sulphate aerosols that have more simple production and decay terms than SOA (Jacob et al., 1997; Barrie et al., 2001). Therefore, only the use of the same global model for different case studies as performed in the present study can clarify differences.

When comparing the models that do not include evaporation of the particles, Kanakidou et al. (2000) calculate a much higher SOA production compared to Griffin et al. (1999b), since the latter assumes the condensation of semi-volatile compounds only on pre-existing SOA and not on primary carbonaceous particles. This assumption leads to much lower pre-existing particle concentrations which can serve as absorptive matter

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for newly formed condensable products. The results of Kanakidou et al. (2000) can be also compared with S2 that considers condensation of SOA only on carbonaceous aerosols. The present study (S2) has been performed with a higher resolution model and with updated, slightly lower, primary carbonaceous particle emissions. Thus S2 results in about 30% lower SOA formation than the earlier estimate. Chung and Seinfeld (2002) also use higher POA emissions by a factor of 2 than this work. Comparison of S2 with S4, considering that condensation occurs also on sulphuric and ammonium aerosols in addition to carbonaceous particles, results in little additional SOA from biogenic VOC but relatively much higher increase of SOA coming from anthropogenic VOC, since this additional aerosol surface is present mainly over anthropogenically affected areas.

The model simulations that consider SOA evaporation give relatively lower global SOA formation estimate than simulations neglecting evaporation. The budget seems to depend strongly on the total aerosol in the model. The higher SOA production calculated by Chung and Seinfeld (2002) compared with case S1 is possibly due to the consideration by these authors of SOA formation from all 3 oxidant reactions of VOC, also considered by Derwent et al. (2003). This difference can also reflect the differences in the number of surrogate species of each model.

3.2. Other sensitivities

In addition to the above described sources of uncertainty in SOA tropospheric budget, we wish to highlight the role of: (1) the temperature dependence of the partitioning coefficient K_i of a compound between the gas and the aerosol phase, (2) the fate of the first generation products of the VOC precursors of SOA and (3) the dependence of the aerosol production and removal on the activity coefficient. For this purpose, simulation S1 has been modified appropriately and has been used as a reference case for simulations S1.1 to S1.5.

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3.2.1. Temperature – cases S1.1 and S1.2

Following the two very similar approaches of Strader et al. (1999) and Andersson-Sköld and Simpson (2001) to evaluate the variation of the same partitioning coefficient with temperature, very large differences up to 10 orders of magnitude in low temperatures are calculated and depicted in Fig. 1. Such differences result in critical discrepancies between the models and need to be reduced to provide a more accurate estimate of the SOA production, especially in high latitudes during winter and at high altitudes in the mid and upper troposphere. To evaluate the errors in the model calculations due to the uncertainty in the enthalpy of vaporization, an additional calculation of the SOA production is made by adopting the ΔH value of 79 KJ mol^{-1} (Andersson-Sköld and Simpson, 2001; case S1.1) that is close to recent data by Pun et al. (2003). The differences of the thus calculated total SOA concentrations (sum of biogenic and anthropogenic, case S1.1) and the reference case S1 are shown in Fig. 6. In general, higher SOA concentrations with decreasing temperature are calculated in S1.1 than in the reference case, since the partitioning coefficient increases faster in S1.1 with decreasing temperature. Near the surface, in areas where temperatures are higher than 298 K the aerosol concentration decreases, as expected from Eq. (18). At temperature lower than 298 K, the partitioning coefficient decreases faster with increasing temperature when the enthalpy of vaporization is higher than the base case, while when the temperature is higher than 298 K the trend is opposite. If we neglect the temperature dependence of the vapour pressure described in (17) ($\Delta H = 0$; case S1.2), the partitioning coefficient remains almost constant over the whole temperature range in the troposphere, but with a slight tendency to increase with increasing temperature, in contrast with the cases S1 and S1.1 where vapour pressure depends on temperature. The calculated concentration differences between the reference case and S1.2 are shown in Fig. 7.

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3.2.2. Secondary oxidation – case S1.3

As mentioned in Sect. 2.2, the gas phase oxidation of the SOA precursor species produce the first generation semi-volatile products that are able to partition between the gas and aerosol phase. These can, in turn, further oxidize in the gas-phase and give secondary semi-volatile products that can also partition. The calculated differences that occur when taking into account the further oxidation of the primary condensable products (case S1.3) compared to our reference case can be seen in Fig. 8. Near the surface, taking into account the formation of the secondary condensable products, leads to higher SOA concentrations compared to the reference case. This happens because the second generation products have higher partitioning coefficients, resulting in higher aerosol yield. On the contrary, in the upper troposphere a decrease of SOA concentration is calculated because of the condensation of the gas-phase condensable species at lower altitudes.

It is remarkable that the simplified chemistry scheme (Fig. 8) does not significantly affect the spatial distribution of the aerosols, since the adopted partitioning coefficients have the same temperature dependence in both simulations. The enhancement of the total aerosol yield (Fig. 6) due to the temperature dependence of K_p displaces the geographical location of the secondary maximum of aerosol mixing ratios towards lower levels (lower altitudes) i.e. at higher temperatures. This reveals the importance of accurate knowledge of the temperature dependence of K_p and thus of the physicochemical parameters of the condensable compounds. The chemical structure and chemical fate of the low vapour pressure products seem to be also very critical for the SOA simulations.

3.2.3. Activity coefficient cases S1.4 and S1.5

The partitioning coefficient used in this study has been measured in chamber studies with almost pure SOA. In the real atmosphere though, the mixed aerosols have non-uniform physicochemical properties. This is taken into account in Eq. (16) by the use of

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the activity coefficient that is calculated in Eq. (19). The model is not very sensitive to that parameter, since a net increase of up to 230 ng m^{-3} in SOA concentration occurs if we neglect the variation of the activity coefficient (ζ_i = 1, case S1.4) compared to the reference case S1. If we assume a stronger influence of the activity coefficient (lower Λ values, case S1.5) a net decrease is calculated and the difference reaches 340 ng m^{-3}. The calculated differences for case S1.4 are shown in Fig. 9, and for case S1.5 in Fig. 10. These simulations add an uncertainty of about ±10% to the estimated SOA global budget.

3.3. Comparison with measurements

Comparison of the model results with observations may identify which simulations and assumptions are more realistic.

Unfortunately, the measurements of carbonaceous aerosols around the world are sparse. Additionally, the comparison of model results with measurements cannot be done with all data available, since the model grid represents the mean concentration of rather large areas. In this respect, it is not appropriate to compare the model with the measurements from a site with high local influence, i.e. the centre of a city. Therefore, we selected the measurements that could be representative of relatively large rural, remote and marine areas. Another uncertainty in the model evaluation with the observations comes from the conversion of organic aerosol mass (OA) that is simulated by the model to the organic carbon (OC) content of the aerosol measured in the field. To convert the model calculated OA concentration to OC concentration we use the global mean ratio OA/OC = 1.3 suggested by Liousse et al. (1996). Note that this ratio is expected to vary spatially but this variation has been neglected here. This is not the case though for black carbon, where the comparison with measurements is direct. Figure 11 compares BC measurements with our model results, including the results from Liousse et al. (1996) and Chung and Seinfeld (2002) where available. No specific trend in all three different models is observed from this figure. All models seem to represent fairly well BC data.

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In the case of organic aerosols (Fig. 12) the amount of observations is more sparse. All model simulations, and particularly S1, underestimate OC concentrations below 1 μg m^{-3} i.e. over relatively clean rural and marine areas. With the actual knowledge, it's difficult to attribute the discrepancy between model results and observations to the primary or the secondary carbon, since it is hard to separate the secondary from the primary carbon in the field measurements. The areas where the model predicts too low OC concentrations are mainly marine areas, suggesting either that the model might have very high removal of organic aerosols or that condensation on sea-salt aerosol (not taken into account in our study) might be of importance for these areas. The results of Chung and Seinfeld (2002) also seem to generally underpredict the measurements, while Liousse et al. (1996) results, even the few available numbers, agree relatively well with the measurements. Both these earlier studies use an almost two times higher source of POA than our study.

An interesting feature one can raise is that since in our model we have similar treatment of POA particles and BC particles, one would expect that their comparison with measurements would follow the same pattern. This is not the case, since the model calculates the BC carbon measurements in remote areas much closer to the measured ones than for OA. This might be an indication that the main problem in the OA calculation is not the primary fraction, but the secondary one. Since the dry deposition of POA and SOA treated in the same way, the difference can be due either to high SOA removal by wet deposition or to low chemical production, or both. It might also be the case that POA has lower deposition removal rates than BC. This issue has to be investigated in the future.

4. Conclusions

A global 3-dimensional chemistry/transport model has been extended to simulate the temporal and spatial distribution of carbonaceous aerosols in the global troposphere with focus on the secondary organic aerosol formation. It also considers the conver-

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sion of primary carbonaceous aerosols from hydrophobic to hydrophilic. The model sensitivity to the input parameters and to the model assumptions has been carefully investigated, since the missing knowledge on SOA formation and properties inhibits an accurate SOA budget estimate.

The global annual production of SOA has been calculated to vary from 2.5 to 44.0 Tg y^{-1} for the biogenically produced SOA and from 0.05 to 2.62 Tg y^{-1} for the anthropogenic SOA. However these values have to be considered as a lower limit, since SOA formation from NO_3 reactions with all VOC and from OH oxidation of biogenic VOC has been neglected, as well as condensation on nitrate, sea-salt and dust pre-existing particles and aerosol water. The SOA distribution presents two maxima: one at the surface, close to the source regions of the precursor VOC, and another in the upper troposphere, close to the tropopause region where temperatures are very low and partitioning coefficients very high. This temperature dependence of the partitioning coefficient is a factor of uncertainty in the model, since it depends on the enthalpy of vaporization of the condensable species that is a highly uncertain variable. The spatial distribution of the SOA changes in the case with increasing enthalpy of vaporization, and displaces the maximum in lower altitudes compared to the reference case, since the partitioning coefficient becomes high enough already in lower altitudes.

According to our sensitivity analysis, the most critical factors of uncertainty studied here for the SOA budget turn out to be the evaporation of pre-existing semi-volatile compounds from the aerosol phase, the aerosol mass on which the gas-phase of the semi-volatile compounds can condense and the temperature dependence of the partitioning coefficient. Another point of uncertainty is the deposition processes, since in our model we use only the mass distribution and not the number or size distribution of the particles. In order to assess the error introduced by these latter uncertainties, a more sophisticated model is needed, considering the evolution of both the physicochemical behaviour and the size distribution in addition to the above analysed factors.

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Table 1. Temperature dependant reaction rates of particle precursor VOC (biogenic and anthropogenic) with OH, O_3 and NO_3 used in the model. P_1, P_2 are the first generation products of the corresponding VOC

	OH		O_3		NO_3	
	A	*B*	*A*	*B*	*A*	*B*
a-pinene	1.21e-11	444	1.01e-15	-732	3.15e-13[a]	841[a]
β-pinene	2.38e-11	357	1.5e-17	–	1.6e-10[a]	-1248[a]
toluene[b]	5.96e-12	–	2.34e-12	-6694	6.8e-17	–
xylene[b]	1.72e-11[c]	–	d	d	3.54e-16[c]	–
a-pin-P_1[e]	4.28e-12	–	0	–	0	–
a-pin-P_2[f]	9.3e-11	–	8.9e-20	–	5.4e-14	–
β-pin-P_1[g]	3.03e-12	–	0	–	0	–
β-pin-P_2[h]	1.7e-11	–	5.0e-21	–	1.1e-15	–
tol-P_1	i	–	0	–	i	–
tol-P_2	i	–	0	–	i	–
xyl-P_1	j	–	0	–	j	–
xyl-P_2	j	–	0	–	j	–

$K=A*\exp(B/T)$, where T is the temperature in Kelvin. Taken from Atkinson (1997) unless noted differently.
–: No temperature dependence.
[a]: Martínez et al. (1998).
[b]: Atkinson (1994).
[c]: Average of *ortho*-, *meta*- and *para*- isomers.
[d]: Average of temperature dependence for *ortho*-, *meta*- and *para*- isomers: (2.4E-13 exp(-5586/T)+5.37E-13 exp(-6039/T)+1.91E-13 exp(-5586/T))/3.
[e]: Treated as pinonic acid. Kwok and Atkinson (1995).
[f]: Treated as pinonaldehyde. Hjorth et al. (1996).
[g]: Treated as pinic acid. Kwok and Atkinson (1995).
[h]: Treated as nopinone. Hjorth et al. (1996).
[i]: Treated as toluene.
[j]: Treated as xylene.

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Table 2. Λ values used for the interactions (Λ_{ij}) between species in carbonaceous aerosols. Note that only the interactions between SOA affect the aerosol production. The subscripts "ins" and "sol" declare the insoluble and the soluble fraction of the corresponding aerosol type, respectively. "Other" stands for non-carbonaceous aerosol

	SOA	OA_{ins}	OA_{sol}	BC_{ins}	BC_{sol}	Other
SOA	1.0	0.8	0.9	0.7	0.8	0.7
OA_{ins}	0.8	1.0	0.8	0.8	0.7	0.8
OA_{sol}	0.9	0.8	1.0	0.7	0.8	0.7
BC_{ins}	0.7	0.8	0.7	1.0	0.8	0.7
BC_{sol}	0.8	0.7	0.8	0.8	1.0	0.8
Other	0.7	0.8	0.7	1.0	0.8	0.7

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Table 3. Partitioning (K) and stoicheiometric (a) coefficients for biogenic and anthropogenic SOA formation

	α-pinene[a]	β-pinene[a]	toluene[b]	xylene[b]	B_b	B_a
a_{i1}	0.125	0.026	0.071	0.038	1.0 [c]	1.0 [c]
K_{i1}	0.088	0.195	0.053	0.042		
a_{i2}	0.102	0.485	0.138	0.167	0	0
K_{i2}	0.0788	0.003	0.0019	0.0014	–	–

[a]: Oxidant i is O_3 (Griffin et al., 1999a).
[b]: Oxidant i is OH and O_3 (Odum et al., 1997a, b).
[c]: Maximum of the precursor species at given temperature.

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Table 4. Outline of simulations performed in this study

Simulation	Description
S1	Partitioning on carbonaceous aerosols, with evaporation, ΔH = 42 KJ mol^{-1}, without oxidation of the first generation semi-volatile products, the hydrophobic to hydrophilic conversion depends on O_3 and H_2O – Sect. 2.4
S1.1	As S1, ΔH = 79 KJ mol^{-1} – Eq. (18)
S1.2	As S1, ΔH = 0 KJ mol^{-1} – Eq. (18)
S1.3	As S1, with oxidation of the primary condensable products – Sect. 2.2
S1.4	As S1, without dependence on the activity coefficient – Eq. (19)
S1.5	As S1, with strong dependence on the activity coefficient – Eq. (19)
S2	As S1, without evaporation of pre-existing SOA
S3	As S1, including the partitioning on sulphuric and ammonium aerosol
S4	As S3, without evaporation of pre-existing SOA

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Table 5. Global annual SOA production performed using the results of chamber experiments, versus the results of the present 3-D global modelling study

Production (Tg yr^{-1})	Case	VOC precursors (number)	Pre-existing particles[a]	Evaporation	Transport of intermediates	Reference
13-24	Present day	Biogenic (30)	No	No	No	Griffin et al., 1999b
61-79	Present day	Biogenic (2)	C	No	No	Kanakidou et al., 2000
16.5-28	Pre-industrial	Biogenic (2)	C	No	No	Kanakidou et al., 2000
11.2	Present day	Biogenic (5)	C	Yes	Yes	Chung and Seinfeld, 2002
63	Present day	Biogenic (1)	C	Yes	Yes	Derwent et al., 2003
7.2 (0.3)[b]	Present day	Biogenic (2) & anthropogenic (2)	C	Yes	Yes	This work – S1
44.0 (2.0)[b]	Present day	Biogenic (2) & anthropogenic (2)	C	No	Yes	This work – S2
13.3 (0.7)[b]	Present day	Biogenic (2) & anthropogenic (2)	CSN	Yes	Yes	This work – S3
44.5 (2.6)[b]	Present day	Biogenic (2) & anthropogenic (2)	CSN	No	Yes	This work – S4

[a]: C: Carbonaceous aerosols, CSN: Carbonaceous, sulphate, methanesulphonate and ammonium aerosols
[b]: Read as: Biogenic VOC contribution to SOA (Anthropogenic VOC contribution to SOA)

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Table 6. Global annual SOA production and burden (from surface up to 10hPa) calculated in all studied cases of this work

	Chem. prod. (Tg y^{-1})		Burden (Gg)	
Case	SOAb	SOAa	SOAb	SOAa
S1	7.2	0.27	47.5	2.2
S1.1	18.3	1.05	115.6	7.8
S1.2	2.5	0.05	13.7	0.5
S1.3	8.8	0.24	54.6	2.1
S1.4	7.7	0.29	51.6	2.5
S1.5	6.6	0.24	41.8	1.9
S2	44.0	2.02	369.8	24.6
S3	13.3	0.70	105.1	6.3
S4	44.5	2.62	356.9	27.3

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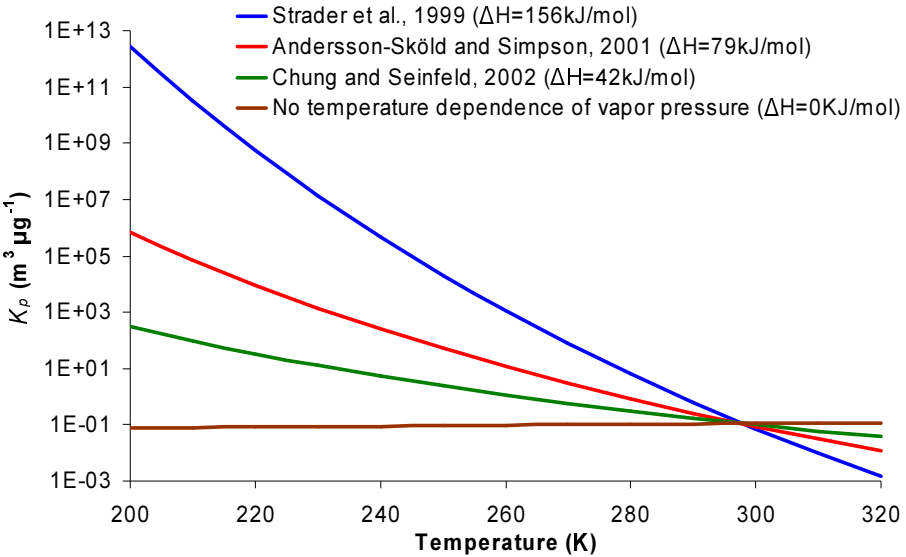

Fig. 1. Variation of K_p with temperature, for the case K_p = 0.11 at 298 K.

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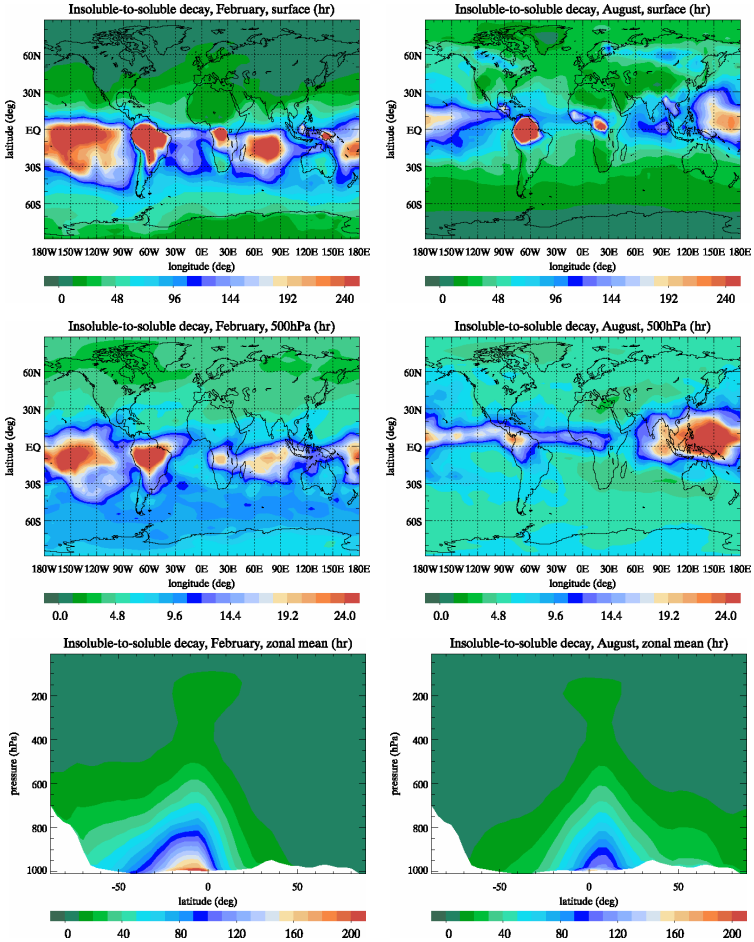

Fig. 2. Calculated lifetimes of hydrophobic primary carbonaceous aerosols for case S1 at surface (top panels), 500 hPa (middle panels) and zonal mean (bottom panels) for February (left panels) and August (right panels).

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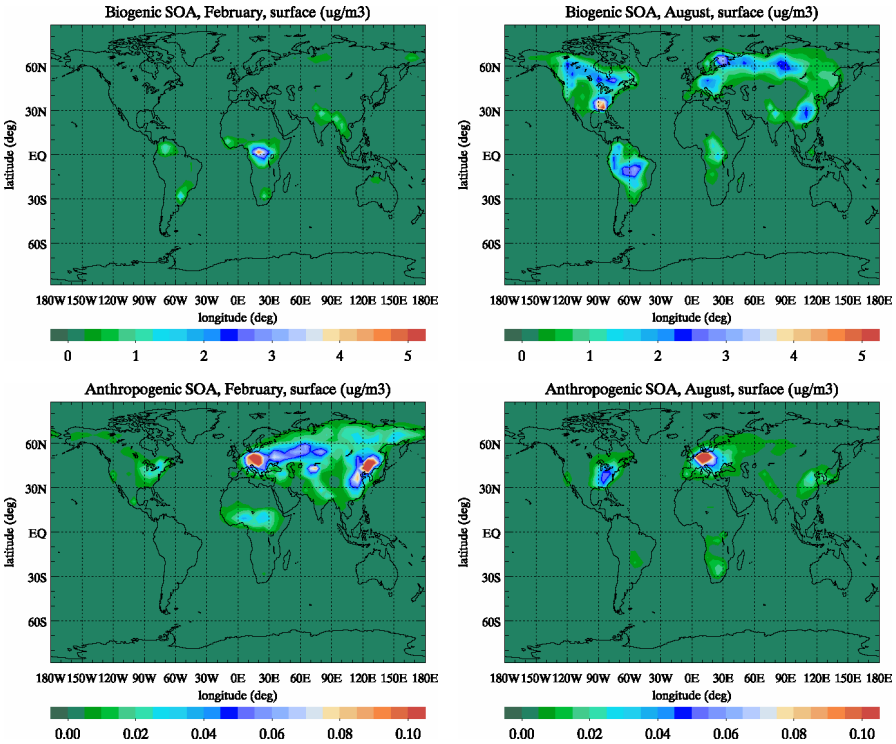

Fig. 3. Calculated surface SOA concentrations for case S1, both biogenic (SOAb (in μg m^{-3}), top panels) and anthropogenic (SOAa (in μg m^{-3}), bottom panels) components, for February (left panels) and August (right panels).

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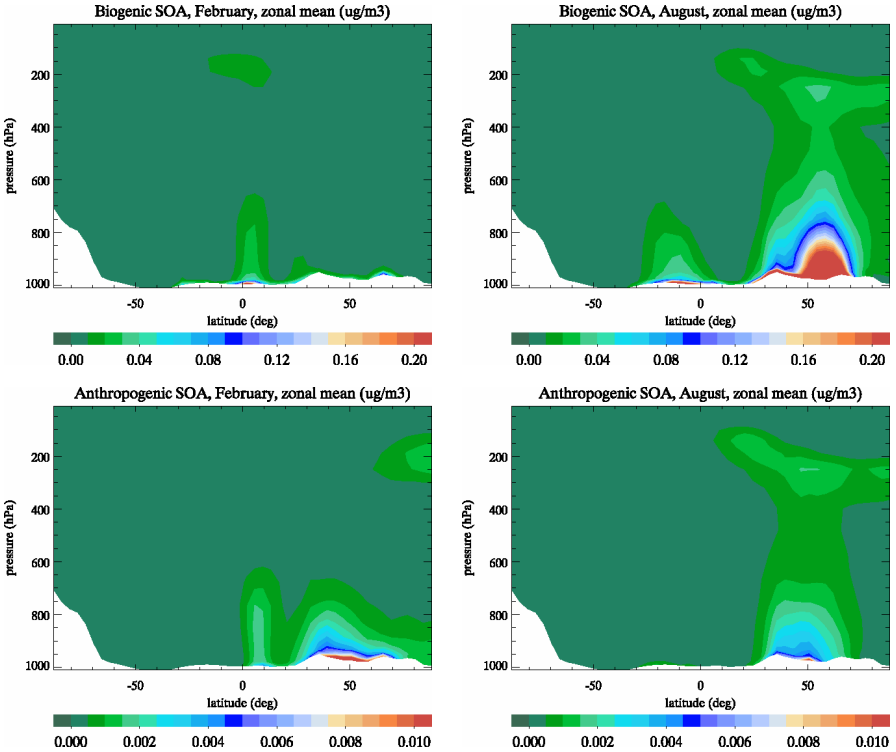

Fig. 4. Calculated zonal mean SOA concentrations for case S1, both biogenic (SOAb (in μg m^{-3}), top panels) and anthropogenic (SOAa (in μg m^{-3}), bottom panels) components, for February (left panels) and August (right panels).

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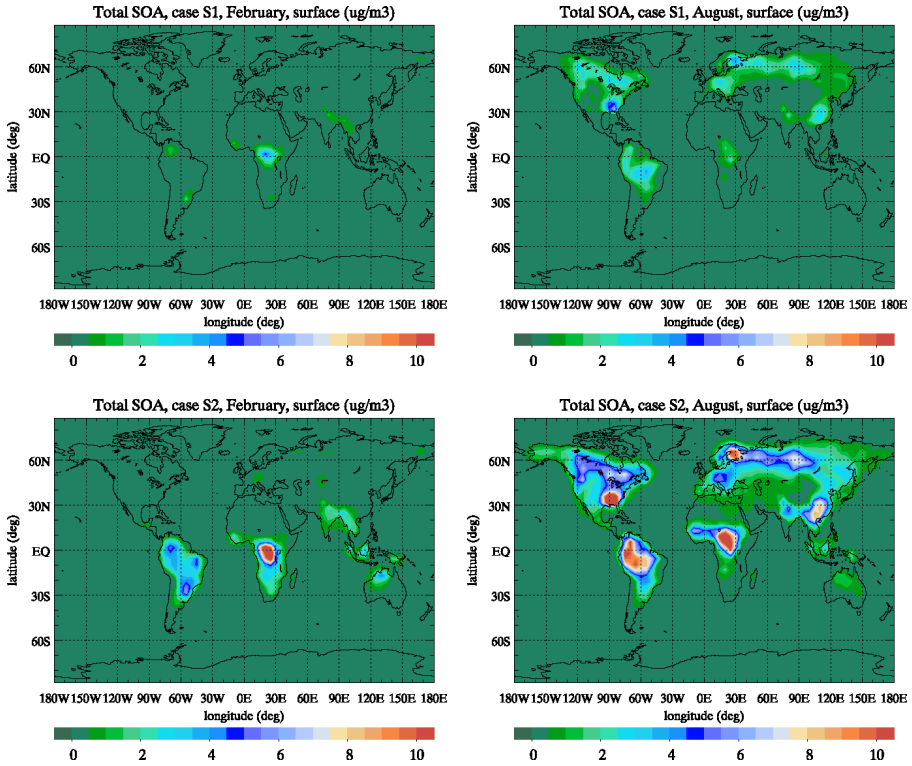

Fig. 5. Comparison of the total SOA concentrations in μg m^{-3} (sum of biogenic and anthropogenic) of cases S1 (top panels), S2 (middle-top panels), S3 (middle-bottom panels) and S4 (bottom panels) for February (left panels) and August (right panels) (continued on next page).

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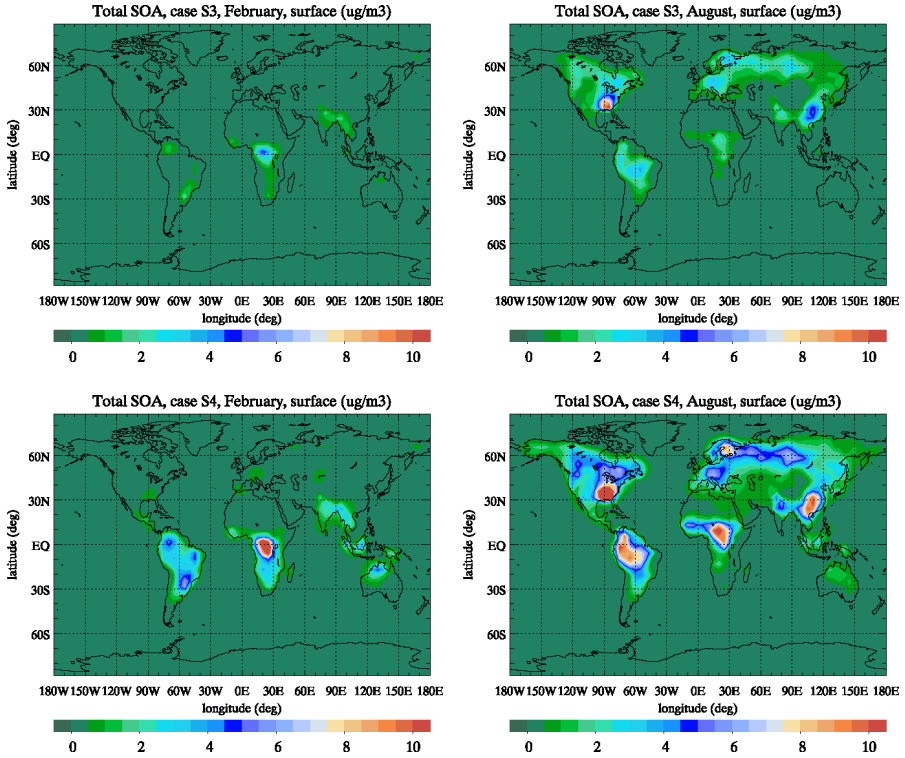

Fig. 5. Continued.

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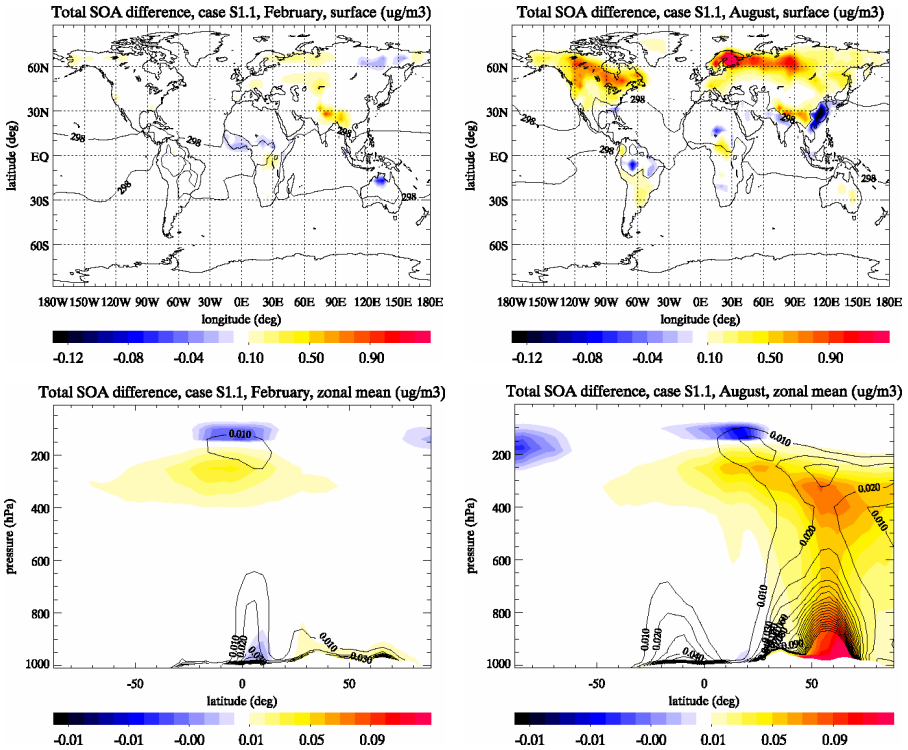

Fig. 6. Calculated differences of the total SOA concentrations in μg m^{-3} (sum of biogenic and anthropogenic) with increased enthalpy of vaporization ΔH (case S1.1) compared to the reference case S1 for February (left panels) and August (right panels), both for surface (top panels) and zonal mean (bottom panels) case. Red means increased SOA concentration with increased enthalpy of vaporization and blue means decreased SOA concentration with increased enthalpy of vaporization. The contours in the surface plates show the area with air temperature equal to 298 K and those in the zonal mean plates show the SOA concentration of the case S1. Note the different scaling between the positive and negative values.

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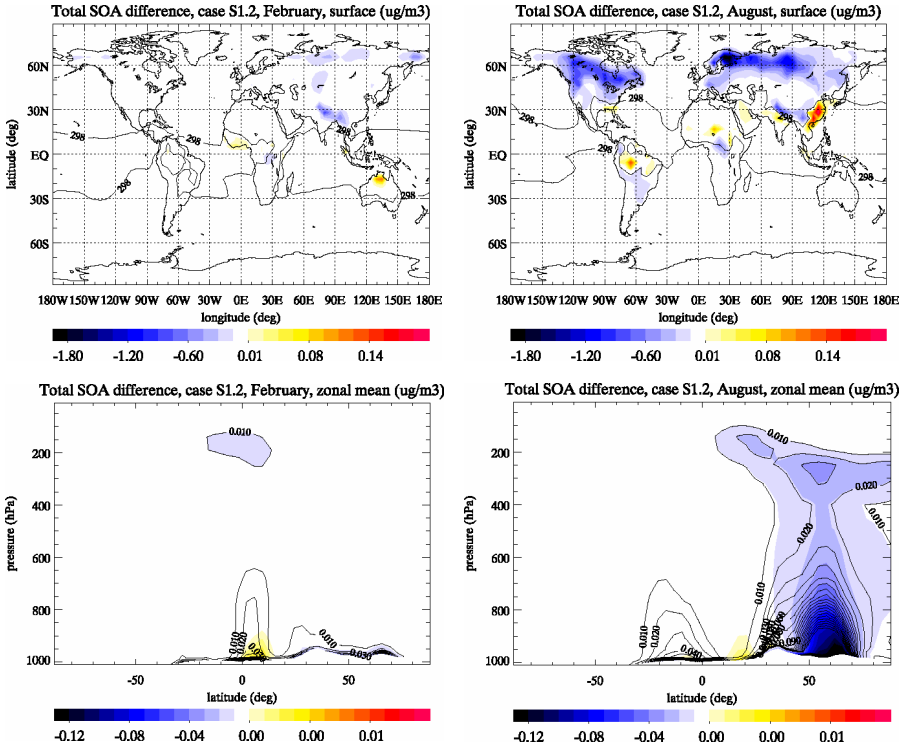

Fig. 7. Calculated differences of the total SOA concentrations in μg m^{-3} (sum of biogenic and anthropogenic) with zero enthalpy of vaporization ΔH (case S1.2) compared to the reference case S1 for February (left panels) and August (right panels), both for surface (top panels) and zonal mean (bottom panels) case. Red means increased SOA concentration with zero enthalpy of vaporization and blue means decreased SOA concentration with zero enthalpy of vaporization. The contours in the surface plates show the area with air temperature equal to 298K and those in the zonal mean plates show the SOA concentration of the case S1. Note the different scaling between the positive and negative values.

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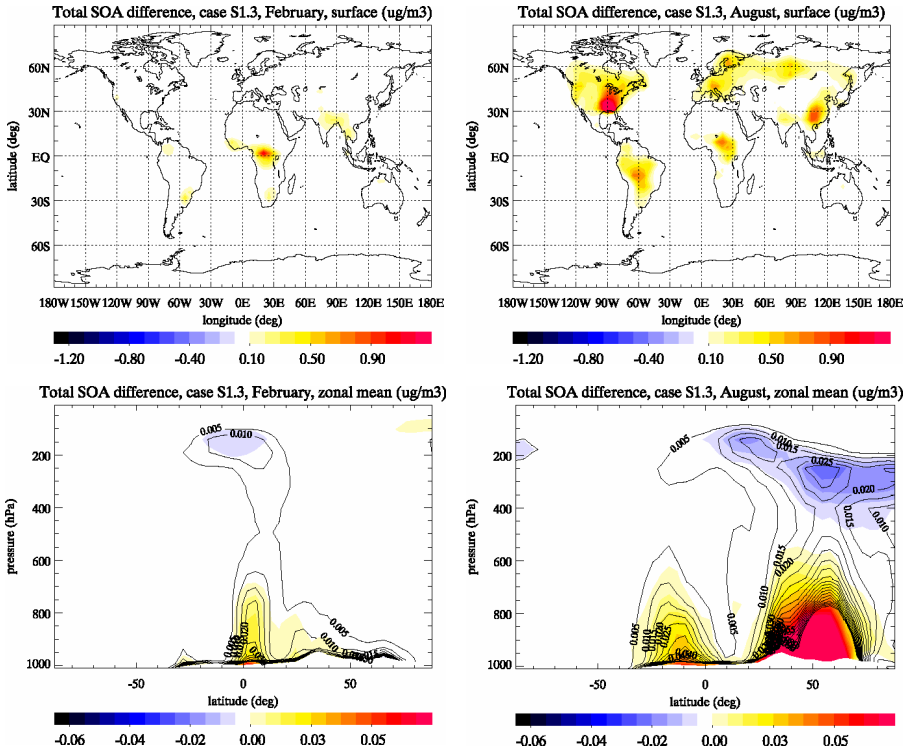

Fig. 8. Calculated differences of the total SOA concentrations in μg m^{-3} (sum of biogenic and anthropogenic) when taking into account the oxidation of the primary oxidation products of the SOA precursor VOC (case S1.3) compared to the reference case S1 for February (left panels) and August (right panels), both for surface (top panels) and zonal mean (bottom panels) case. Red means increased SOA concentration when we take into account the oxidation of the primary products and blue means decreased SOA concentration when we take into account the oxidation of the primary products. The contours in the zonal mean plates show the SOA concentration of the case S1.

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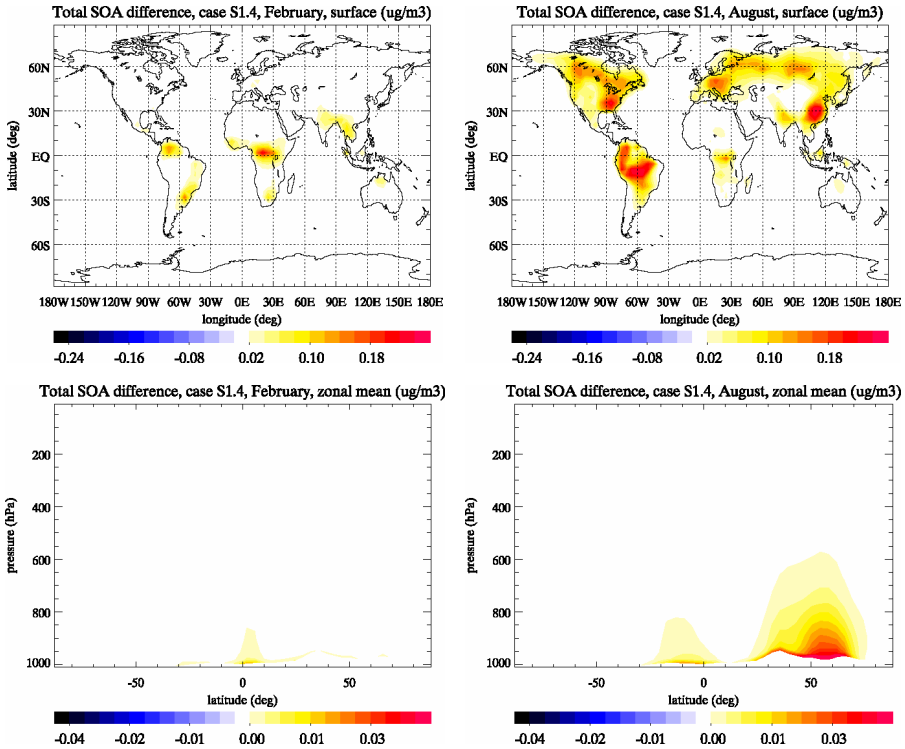

Fig. 9. Calculated differences of the total SOA concentrations in μg m^{-3} (sum of biogenic and anthropogenic) when neglecting the activity coefficient influence (case S1.4) compared to the reference case S1 for February (left panels) and August (right panels), both for surface (top panels) and zonal mean (bottom panels) case. Red means increased SOA concentration when we neglect the activity coefficient influence and blue means decreased SOA concentration when we neglect the activity coefficient influence.

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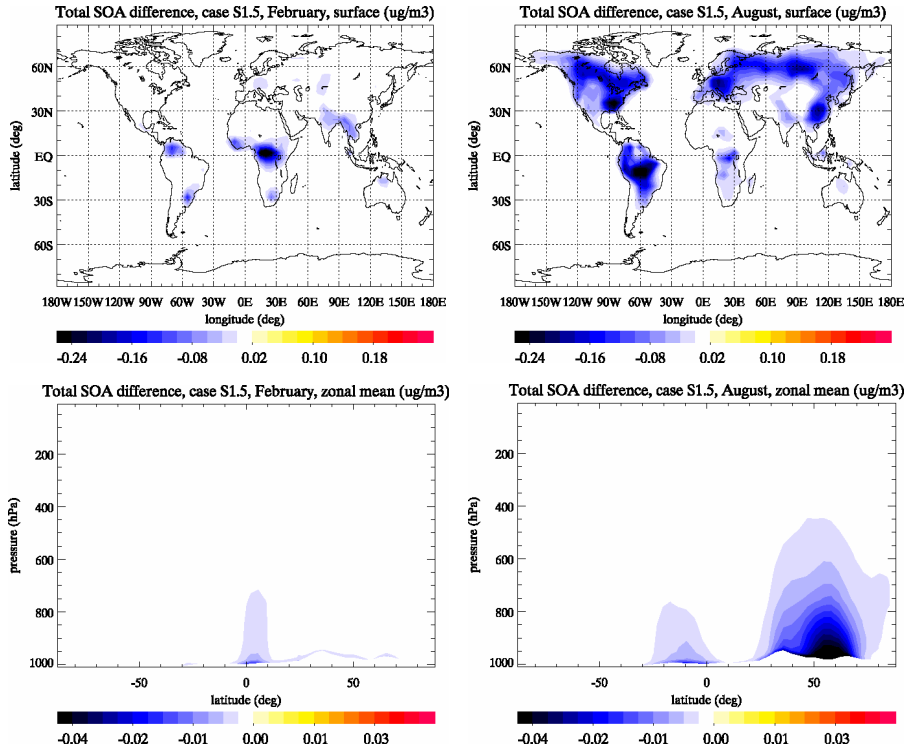

Fig. 10. Calculated differences of the total SOA concentrations in μg m^{-3} (sum of biogenic and anthropogenic) when we assume strong activity coefficient influence (case S1.5) compared to the reference case S1 for February (left panels) and August (right panels), both for surface (top panels) and zonal mean (bottom panels) case. Red means increased SOA concentration when we assume strong activity coefficient influence and blue means decreased SOA concentration when we assume strong activity coefficient influence.

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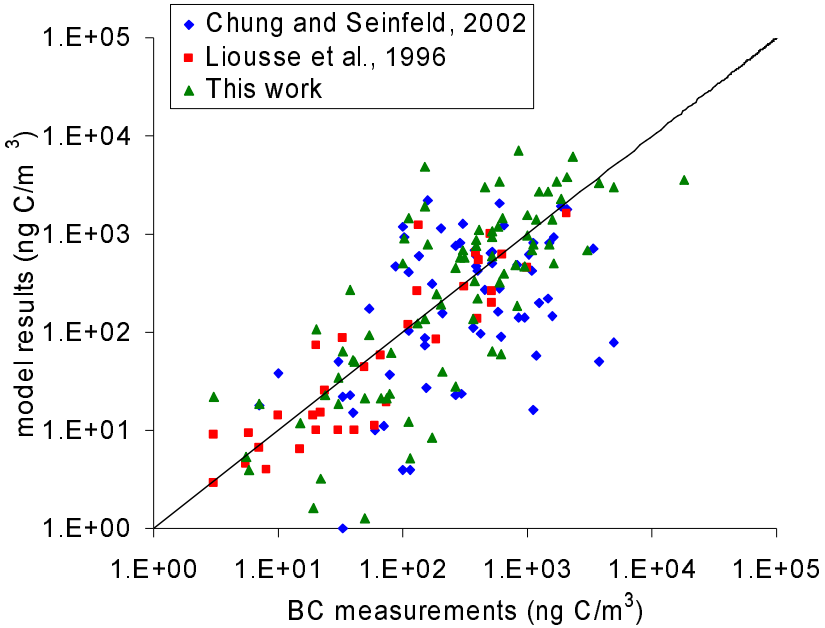

Fig. 11. Comparison of black carbon measurements with model results (cases S1–S4) and other models results (Liousse et al., 1996; Chung and Seinfeld, 2002). The continuous line shows the 1:1 relationship between model results and measurements (Andreae et al., 1984; Dzubay et al., 1984; Ohta and Okita, 1984; Cachier et al., 1986; 1989; 1990; 1994; Japar et al., 1986; Wolff et al., 1986; Hansen et al., 1988; 1991; Noone and Clarke, 1988; Clarke, 1989; Mukai et al., 1990; Heintzenberg and Bigg, 1990; Jennings and O'Dowd, 1990; Hopper et al., 1991; Yaaqub et al., 1991; Jennings et al., 1993; Polissar, 1993; Raunemaa et al., 1993; 1994; Chow et al., 1994; Heintzenberg and Leck, 1994; Parungo et al., 1994; Bodhaine, 1995; Berner et al., 1996; Liousse et al., 1996; Lowe et al., 1996; Pio et al., 1996; Smith et al., 1996; Bahrmann and Saxena, 1998; Wolff and Cachier, 1998; Bizjak et al., 1999; Castro et al., 1999; Chýlek et al., 1999; Hitzenberger et al., 1999; Zappoli et al., 1999; Kaneyasu and Murayama, 2000; Kim et al., 2000; Novakov et al., 2000; Puxbaum et al., 2000).

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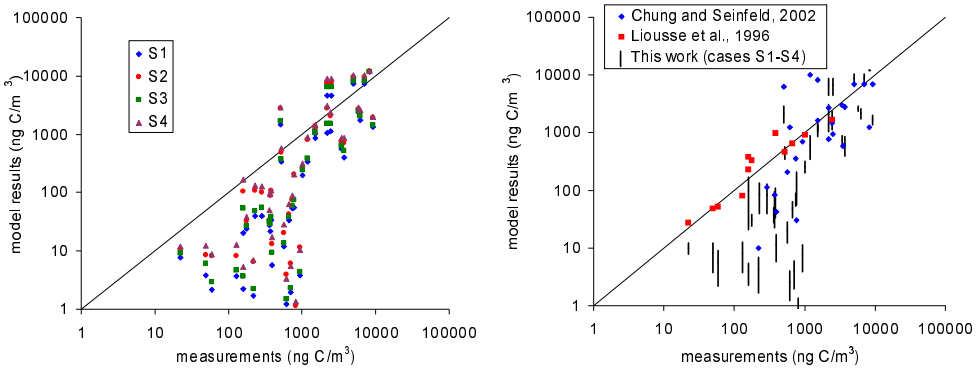

Fig. 12. Comparison of organic carbon measurements with model results (cases S1–S4, left panel) and other models results (Liousse et al., 1996; Chung and Seinfeld, 2002, right panel). The continuous line shows the 1:1 relationship between model results and measurements (Hidy et al., 1974; Hoffmann and Duce, 1974; 1977; Ketseridis et al., 1976; Chesselet et al., 1981; Andreae, 1982; 1983; Andreae et al., 1984; Dzubay et al., 1984; Ohta and Okita, 1984; Cachier et al., 1986; 1989; 1990; 1994; Japar et al., 1986; Wolff et al., 1986; Clarke, 1989; Mukai et al., 1990; Novakov and Penner, 1993; Chow et al., 1994; Liousse et al., 1996; Novakov et al., 1997; Castro et al., 1999; Molnár et al., 1999; Zappoli et al., 1999; Kim et al., 2000; Puxbaum et al., 2000).

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